Chemical characterization and oxidative stability of castor oil grown in Morocco

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Abstract
Seed oil of Castor bean \( (Ricinus communis \, L) \) grown in Morocco were analyzed for their main chemical composition and for their oxidative stability. Gas chromatography revealed that the major fatty acids were ricinoleic, linoleic, and oleic acids (75.0%, 9.7%, and 7.7% respectively). Seed oil was also found to be rich in sterols (2210 mg/kg) with a predominance of \( \beta \)-sitosterol (1041 mg/kg). The tocopherols marker \( \delta \)-tocopherol accounted for 43.1 mg/kg. Oxidative stability of castor oil was measured at 110 °C at the air flow rate of 20 L/hw, castor oil was more stable than many other oils with 35.5 h. The results achieved suggest that the castor bean might be an important source of vegetable oil for industrial uses.

Keywords: Ricinus communis L.; Cold-press oil; Fatty acid; Morocco; Seed oil

1. Introduction
The castor plant botanical name is \( Ricinus communis \, L \) of the family Eurphorbiaceae, a plant indigenous to many parts of the world. Castor plant from which castor beans and oil are subsequently derived grows naturally over a wide range of geographical regions and may be activating under a variety of physical and climatic regimes. The plant is however essentially a tropical species, although it may grow in temperate regions [1]. Literature revealed that Castor beans contains about 30-35 percent oil [1-2]. A crude Castor oil is a pale straw colour [1-2] but turns colourless or slightly yellowish after refining and bleaching. The crude oil has distinct odour, but it can easily be deodorized in the refining process. Like any other vegetable oils and animal fats, it is a triglyceride, which chemically is a glycerol molecule with each of its three hydroxyl group esterified with a fatty acid. Its major fatty acid is the monounsaturated, hydroxylated 12-hydroxy, 9-octadecenoic acid, known as ricinoleic acid [3]. Castor oil differs from other fats in solubility and some other properties - high density, big viscosity, and high acetylic number [4]. Castor oil and its derivatives are used in the production of paints, varnishes, lacquers, and other protective coatings, lubricants and greases, hydraulic fluids, soaps, printing inks, linoleum, oil cloth and as a raw material in the manufacturing of various chemicals sebacic acid and undecylenic acid, used in the production of plasticizer and Nylon [5].


many ways, castor oil is a very unique substance. While most of us are familiar with its use as a remedy for constipation, folk healers have used castor oil to treat a wide variety of conditions. Its effectiveness is probably due in part to its peculiar chemical composition [6]. India is the world’s largest exporter of castor oil; other major producers being China and Brazil [7]. The characteristics of castor oil from other countries such as Brazil, Nigeria, India, China and Spain had been studied. However, no one has been carried out on castor oil of Morocco. In our knowledge, this study is the first report on the chemical composition and oxidative stability of the Moroccan cold pressed castor bean oil.

2. Materials and methods

2.1. Plant material and chemicals

Castor seeds were collected from Berrchid city in the region of Chaouia Ouardigha situated in central Morocco (33°16'03.0"N 7°34'59.5"W). Seeds were harvested in June 2014. After harvest, the seeds were stored at 4 °C until processed.

All the reagents were of analytical or HPLC grade. Isooctane and isopropanol used as HPLC mobile phase and cyclohexane used for extinction coefficient determination were purchased from Professional Labo (Casablanca, Morocco).

2.2. Castors seed oil analysis

**Oil extraction**: Extraction was carried out using screwless cold presses (IBG Monforts Oekotec GmbH, Monchengladbach, Germany). Oil samples were stored at 4 °C and protected from sunlight prior analysis.

**Fatty acid composition** was determined using method ISO 5508 [8]. Before analysis, fatty acids (FAs) were converted to fatty acid methyl esters (FAMEs) by shaking a solution of 60 mg oil and 3 mL of hexane with 0.3 mL of 2N methanolic potassium hydroxide. FAs were analyzed by gas chromatography using a Varian CP-3800 (Varian Inc.) chromatograph equipped with a FID. The column used was a CP-Wax 52CB column (30 m×0.25 mm i.d.; Varian Inc., Middelburg, The Netherlands). The carrier gas was helium and the total gas flow rate was 1 mL/min. The initial and final column temperature was 170 °C and 230 °C, respectively, and the temperature was increased by steps of 4°C/min. The injector and detector temperature was 230°C. Data were processed using a Varian Star Workstation v 6.30 (Varian Inc., Walnut Creek, CA, USA). Results were expressed as the relative percentage of each individual FA present in the sample.

**Sterol composition** was determined using method ISO 6799 [9], after trimethylsilylation of the crude sterol fraction, using a Varian 3800 instrument equipped with a VF-1 ms column (30 m 9 0.25 mm i.d.) and helium (flow rate 1.6 mL/min) as carrier gas, column temperature was isothermal at 270°C, injector and detector temperature was 300°C. Injected quantity was 1 µL for each analysis. Data were processed using Varian Star Workstation v 6.30 (Varian Inc., Walnut Creek, CA, USA).

**Tocopherols composition** was determined using the method ISO 9936 [10]. High performance liquid chromatography (HPLC) was used for the determination of tocopherols, using a solution of 250 mg of oil in 25 mL of n-heptane. Tocopherols were analyzed by HPLC using Shimadzu CR8A instruments (Champ sur Marne, France) equipped with a C18-Vari column (25 cm×4 mm; Varian Inc., Middelburg, The
Netherlands). Detection was performed using a fluorescence detector (excitation wavelength 290 nm, detection wavelength 330 nm). Eluent used was a 99:1 iso-octane/isopropanol (V/V) mixture, flow rate of 1.2 mL/min.

**Oxidative stability of seed oils**, Induction time was determined using the method ISO 6886 [11]. The oxidative stability was evaluated by the Rancimat method. Stability was expressed as the oxidative induction period (IP, hours) measured at 110 °C on a Rancimat 743 (Metrohm Co, Basel) apparatus using 3 g of oil sample with an air flow of 20 L/h. Volatile oxidation products were stripped from the oil and dissolved in cold water, whose conductivity increased progressively. The time taken to reach a level of conductivity was measured.

3. Results and Discussions

3.1. Fatty Acid Composition

The fatty acid composition is an essential indicator of the nutritional value of the oil. Table 1 shows the fatty acid composition of Castor seed oil. The most predominant fatty acid was Ricinoleic acid, with a mean value of 75%. In addition to Ricinoleic acid, seed oil of Castor contained low amount of linoleic acid (9.7%) and Oleic acid (7.7%). The seed oil also contains saturated fatty acid especially palmitic and stearic acids. The level of stearic acid was 2.7% and higher than the amount of palmitic acid 2.5%. The polyunsaturated (PU) fatty acids of the oil amounted to 10.7% of the total fatty acid, while the monounsaturated (MU) and saturated (SA) fatty acids amounted to 82.7% and 5.2%, respectively. The ratio of unsaturated/saturated fatty acid of Castor seed oil was 17.9.

Ricinoleic acid, the active component of castor oil, is a gastropathic agent that has been used as a cathartic substance. Several reports describe the absorption of ricinoleic acid [12-13] and its effects on intestinal motility [14].

The Brazilian castor oil contains the highest ricinoleic acid [15]. In contrary to our sample that contain the lowest ricinoleic acid content, the saturated fatty acid content was the highest for the Moroccan sample (5.2%) and the lowest was for the Indian one, the highest unsaturated fatty acid content was 98.3% [16]. This is because sample from India contains no oleic and linolenic acid that make the sample from Morocco more unsaturated due to the content of polyunsaturated fatty acids (PUFA).

**Table 1.** Castor seed oil fatty acid composition (%).

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Morocco</th>
<th>Nigeria</th>
<th>Malaysia</th>
<th>Brazil</th>
<th>India</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic; C16:0</td>
<td>2.5</td>
<td>1</td>
<td>1.3</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Stearic; C18:0</td>
<td>2.7</td>
<td>1</td>
<td>1.2</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Oleic; C18:1</td>
<td>7.7</td>
<td>3</td>
<td>5.5</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>Linoleic; C18:2</td>
<td>9.7</td>
<td>4.2</td>
<td>7.3</td>
<td>4.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Linolenic; C18:3</td>
<td>1</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Ricinoleic; C18:1OH</td>
<td>75.0</td>
<td>89.5</td>
<td>84.2</td>
<td>90.2</td>
<td>94.0</td>
</tr>
<tr>
<td>SFA</td>
<td>5.2</td>
<td>2.3</td>
<td>2.5</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td>UFA</td>
<td>93.4</td>
<td>97.7</td>
<td>97.5</td>
<td>97.6</td>
<td>98.3</td>
</tr>
</tbody>
</table>
3.2. Sterol Composition

The most studied fraction of the unsaponifiable matter is that of sterols, which is frequently analyzed for tracking commercial frauds [17–18]. This fraction has been considered as the major unsaponifiable fraction in many oils. Furthermore, the concentration of sterols has been reported to be little affected by environmental factors and/or by cultivation of new breeding lines [19]. The composition of the sterol fraction is shown in Table 2.

Results from the quantitative analysis of sterols from Castor (expressed in mg/kg of oil) showed that the major sterol of the oil is β-sitosterol (1040 mg/kg oil), which amounted to 47.1% of the total amount of sterols. Stigmasterol (406.6 mg/kg oil), Δ-5 Avenasterol (357.9 mg/kg oil), and Campesterol (249.7 mg/kg oil) were presented, with about 18.4, 16.2 and 11.3% of the total sterols, respectively.

Among the minor sterols, Δ-7 Avenasterol (8.8 mg/kg oil), Δ-7 Stigmastenol (4.4 mg/kg oil), and Cholesterol (4.4 mg/kg oil) amounted to about 1% of the total amount of sterols.

β-Sitosterol content of Castor oil was found higher than that reported in Spanish one (43.5%) [20], but similar to the Austrian one [21]. Δ-5 Avenasterol, Stigmastero and campesterol were most abundant sterol compounds after β-sitosterol in Spanish and Austrian Castor oil. Δ-5 Avenasterol, Stigmasterol and Campesterol content of Spanish and Austrian oil were found to be (25.2, 22.5 and 6.9%) and (17.5, 21.9 and 7.6%) respectively. Δ-5 Avenasterol content of Castor oil was lower than Spanish and Austrian oil [20-21]. Stigmasterol was also lower than Spanish and Austrian oil. But Campesterol level of Moroccan Castor oil was higher than those of the values reported by Velasco and Lechner [20-21]. The total sterol content in castor seed oils was 2209.8 mg kg⁻¹ oil. This value was higher than that determined by Velasco (1520 mg kg⁻¹ oil) [20] but lower than the Austrian one (2473 mg kg⁻¹ oil) [21].

The total sterol contents in castor seed oils was higher than other cold pressed oils like almonds, Brazil nuts, hazelnuts, pecans, pine nuts, pistachios and walnuts (800 to 1600 mg Kg⁻¹ oil). And it’s very close to that of nigella seed oil (1993–2887 mg/kg) [22], but it’s lower than that of soybean and sunflower (2500-4180 and 3250-5150 mg/kg) [23].

Phytosterol has good effectiveness in decreasing serum low-density lipoprotein (LDL) cholesterol levels that could be effective in protecting against cardiovascular diseases, thus it can be used to improve the functional foods.

Table 2: Castor seed oil Sterol composition.

<table>
<thead>
<tr>
<th></th>
<th>Our results</th>
<th>Spain (%)</th>
<th>Austria (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/kg</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Cholesterol</td>
<td>4.41</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Campesterol</td>
<td>249.7</td>
<td>11.3</td>
<td>6.9</td>
</tr>
<tr>
<td>Stigmasterol</td>
<td>406.6</td>
<td>18.4</td>
<td>22.5</td>
</tr>
<tr>
<td>β-sitosterol</td>
<td>1040.8</td>
<td>47.1</td>
<td>43.5</td>
</tr>
<tr>
<td>Δ-5 Avenasterol</td>
<td>357.9</td>
<td>16.2</td>
<td>25.2</td>
</tr>
<tr>
<td>Δ-7 Avenasterol</td>
<td>8.83</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Δ-7 Stigmastenol</td>
<td>4.41</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Total sterol [mg/kg]</td>
<td>22109</td>
<td>-</td>
<td>1520.4</td>
</tr>
</tbody>
</table>
3.3. Tocopherol Composition

Because of the critical role of the tocopherols in nutrition and their relative instability, qualitative and quantitative analyses are very important. To the authors’ knowledge it is the first time that tocopherol composition of cold press Castor oil has been evaluated.

Tocopherol content of castor seed oil is presented in Table 3. Total tocopherol content of castor seed oil (183 mg/kg) is much lower than that of Argan oil (850 mg/kg) [24] and Cactus (946 mg/kg) [23], but close to the olive oil (220 mg/kg), the major tocopherol found in castor oil is γ-tocopherol. It represents 52.73% of total tocopherols, whereas δ- tocopherol represents only 43.09% and α-tocopherol 2.84%. β-tocopherol represents only 1.35%. Castor, Cactus and Argan are the richest source of γ-tocopherol a major difference with olive oil where α-tocopherol is the major tocopherol [23].

Tocopherol compounds are used in food, cosmetics and pharmaceutical industries [25]. Tocopherol protects unsaturated fatty acids from oxidation in the extracted oils, particularly at high temperature operations [26]. α-tocopherol is recommended for human and animal consumption because it has a higher biological activity than other tocopherols, but γ and δ-tocopherol are the tocopherol forms with greater in vitro antioxidant capacity [27]. They avoid the oxidation of vitamin A, β-carotene and essential fatty acids [28]. Since these are the main tocopherols present in castor seeds, selection for increased tocopherol content may contribute to castor oils with enhanced oxidative stability.

Table 3. Castor seed oil Tocopherol composition.

<table>
<thead>
<tr>
<th>Tocopherols [mg/kg]</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>δ</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor</td>
<td>2.8</td>
<td>1.3</td>
<td>52.7</td>
<td>43.1</td>
<td>183</td>
</tr>
<tr>
<td>Cactus</td>
<td>21</td>
<td>-</td>
<td>856.1</td>
<td>70.95</td>
<td>946</td>
</tr>
<tr>
<td>Argan</td>
<td>57</td>
<td>2.5</td>
<td>773</td>
<td>75</td>
<td>880</td>
</tr>
<tr>
<td>Olive</td>
<td>193</td>
<td>10.2</td>
<td>2.5</td>
<td>22</td>
<td>220</td>
</tr>
</tbody>
</table>

3.4. Oxidative stability

Oxidation of lipid is a major cause of deterioration in the quality of oils. It is the cause of important deteriorative changes in their chemical, sensory and nutritional properties. Preservation of castor seed oil has never been investigated, so far. To get a complete picture of castor seed oil oxidative stability, we decided to determine the induction period by Rancimat test, an instrument for automatic determination of the oxidation stability of oils and fats. Induction time of castor seed oil, evaluated by the Rancimat accelerated method, was found to be 35.5 hour at 110°C. At the same temperature, we found the Rancimat induction time of 31, 28.5, 27 and 17 hours for Argan, olive, sesame and nigella oils, respectively. Our results show that the stability of castor seed oil to oxidation is higher than that of argan, olive, sesame and nigella oils. Castor seed oil stability could be attributed to the presence of Ricinoleic, molecule that does not oxidize easily.

Table 4 Moroccan oil oxidative stability (h).

<table>
<thead>
<tr>
<th>Rancimat (h)</th>
<th>Castor</th>
<th>Nigella</th>
<th>Olive</th>
<th>Argan</th>
<th>Sesame</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.5 ± 4</td>
<td>17 ± 2</td>
<td>27 ± 3</td>
<td>31 ± 2</td>
<td>28.5 ± 0.5</td>
<td></td>
</tr>
</tbody>
</table>
4. Conclusion
The cold-pressing procedure involves neither heat nor chemical treatments, and it is becoming an interesting substitute for conventional practices because of consumers’ desire for natural and safe products. Improved knowledge on the composition of *Ricinus communis* L seed oil would assist in efforts to achieve industrial application of this plant. Data about cold pressed Castor seed oil are very few. The high Ricinoleic acid content makes the oil valuable. Tocopherols and sterols, at the level estimated, guarantee the use the oils in cosmetics industry.

References